# Removal of Copper and Cadmium from industrial effluents using the mixed adsorbent in batch study

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**Abstract :** The present work researches the removal of Cu & Cd ions using mixed adsorbent prepared by blending activated charcoal and bone charcoal in 1: 1 ratio for batch and continuous flow operation. The adsorption mechanism follows a chemisorption process due to the synergistic effect associated by contribution of high surface area from the activated charcoal (1600 $m^2$/g) and negative charge from the bone charcoal. The potential capacity of the mixed adsorbent as a minimal effort material for the removal of Cu (II) and Cd (II) from the prepared synthetic metal ion solution was studied by optimizing various parameters in the batch study. The batch adsorption studies have been carried out for 2 hours considering all the 6 parameters by optimizing each of them. The effect of pH, temperature, initial metal concentration, agitation rate, adsorbent dose and contact time were studied with respect to reaction time until the achievement of equilibrium. The maximum removal for Cu (II) is 97.21% and Cd (II) is 78.76% obtained at 2 hrs for pH 6. The % removal for Cu varies from 87.16 to 99.74% at an adsorbent dosage of 5 g, pH 6, initial metal ion concentration of 50 mg/l, with an agitation rate of 180 rpm, and at a temperature of 25°C. Similarly for Cd (II) it varies from 70.23 to 88.4% at 5 g respectively at the same operating conditions.
**Keywords:** Activated charcoal, Bone charcoal, mixed adsorbent, Agitation rate, Metal ion Concentration, Contact time, adsorbent dosage.

## 1.   Introduction

The contamination of wastewater by toxic heavy metallic cations is a worldwide environmental problem. A number of techniques such as filtration, reverse osmosis; chemical precipitation, ion exchange, electro-deposition and adsorption have been used to remove the toxic metals from aquatic environment with varying degree of success. All these methods have inherent advantages and limitations [1]. Natural zeolites are hydrated aluminosilicate minerals of a porous structure with valuable physicochemical properties, such ascation exchange, molecular sieving, catalysis and sorption. The use of natural zeolites for environmental applications is gaining new research interests mainly due to their properties and significant worldwide occurrence. Application of natural zeolites for water and wastewater treatment has been realised and is still a promising technique in environmental cleaning processes. In the past decades, utilisation of natural zeolites has been focussed on ammonium and heavy metal removal[26-43] due to the nature of ion exchange and some review

papers have been appeared [2]. Molecular sieves are widely applied in catalysis, adsorption, and separation, as these processes benefit from their highly ordered channels and ion exchange abilities. Molecular sieves are usually prepared using hydrothermal or solvothermal synthesis methods. Moreover, the challenges associated with novel approaches for the synthesis of molecular sieves with exotic structures and properties continue to be of great importance in the field of molecular sieve materials [3]

Among all environmental pollutions, water pollution by the industrial waste which consists of toxicheavy metals is serious. Hazardous heavy metals present in industrial wastes are copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), chromium (Cr), mercury (Hg) and others. Heavy metals are toxic in nature because of their accumulation in living tissues and environment. Metal cleaning and plating baths, pulp, paper board mills, printed circuit board production, wood pulp production, fertilizer industry etc. are releasing copper into the environment [4]. Copper and its compounds are ubiquitous in nature and will bind to natural organic materials and soil particles, and hence commonly found in surface water. An ultra-trace amount of copper is essential for living organisms. According to Safe Drinking Water act, copper has a permissible limit of 1.3mg/L in drinking water [5]. Beyond these levels, in human beings it causes stomach upset and ulcer, mental retardation, liver and brain damage and so on [4]. Therefore the safe and effective removal of copper from contaminated fresh waters is a significant environmental issue of global concern. Many conventional methods have been developed for the removal of heavy metals from effluents such as sedimentation, ion exchange, membrane filtration, electrochemical processes, chemical precipitation, reverse osmosis and solvent extraction. But these methods are expensive or inefficient when the concentrations of metals are low (below 100ppm) and there is generation of large quantities of wastes. Development of eco-friendly, efficient and low - cost processes is the need of the hour and in this aspect, adsorption is a versatile technology with the advantages of high efficiency and selectivity for adsorbing metals in low concentrations, recycling of the adsorbent and minimization of the sludge generation.

## 2. Materials and methods

### 2.1 Methods and Experimental Analysis

This section gives an overview of methods and experimental analysis involved in the preparation of the mixed adsorbent, characterization of the adsorbent, procedure for adsorption in batch study. Rotary shaker (Spectra Lab instruments Private Ltd & Industrial Research (Delhi) Model HM8T) was used for agitating the solutions containing the mixed adsorbent along with the metal ion solution. Atomic Absorption Spectrophotometer (Thermo Scientific ICE 3000 series) was used to measure concentration (sample analysis) of Cu (II) & Cd(II) before and after adsorption.

### 2.1.1 Preparation of the mixed adsorbent

The mixed adsorbent (Activated Charcoal, AC + Bone charcoal, BC) was prepared in 1:1 ratio and the sieve analysis (SELEC XT 264, AIMIL company ltd)  was carried out in a rotary sieve shaker to determine the particle size of the mixed adsorbent.  The average pore size of the mixed adsorbent was obtained as 572.2 nm.

### 2.1.1.1 Working of the Particle Size Analyzer

The Particle size analyzer works on the principle of Dynamic Light Scattering where He- Ne Laser acts as a light source. There should be Brownian motion in the solution for the uniform distribution of the particle size. The Zetasizer Nano series performs size measurements using a process calledDynamic Light Scattering (DLS). Dynamic Light Scattering (also known as PCS- Photon Correlation Spectroscopy) measures Brownian motionand relates this to the size of theparticles. It does this by illuminating the particles with a laser and analyzing theintensity fluctuations in the scattered light. Figure 1 indicates the pore size distribution of the mixed adsorbent. Table 1 indicates the Peaks, % Intensity and Standard deviation for the mixed adsorbent.
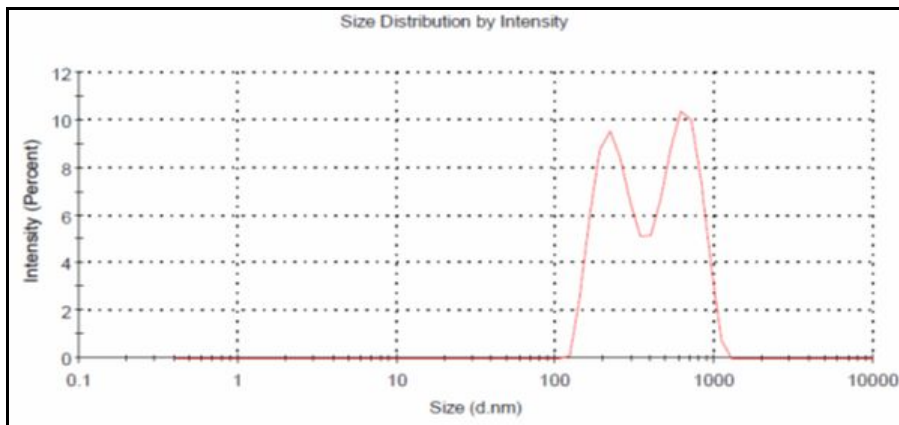
**Fig 1 Pore size distribution of the mixed adsorbent**

(Ref of fig 1: ZetaSizer nano user manual, MAN0485 Issue1.1 April 2013; Malvern Instruments Ltd, Malvern, United Kingdom)

Z-Average (d.nm): 572.2
Poly Dispersity Index (PDI) : 0.676
Intercept: 0.961

**Table 1 Peaks, % Intensity and St. Deviation for the mixed Adsorbent**

| Peak | Size (d.nm) | % Intensity | Standard Deviation |
|---|---|---|---|
| Peak 1 | 613.0 | 55.3 | 180.7 |
| Peak 2 | 232.9 | 44.7 | 58.16 |
| Peak 3 | 0.000 | 0.0 | 0.000 |

**2.2 Characterization of the mixed Adsorbent**

Physical Characterization such as Proximate and Ultimate analysis are done through (ASTM Distillation standards 2009) [6]. FTIR analysis, BET analyses were carried out to determine the physico-chemical properties, different functional groups available for adsorption and surface area of the adsorbent.

**2.2.1 Proximate Analysis**

Proximate analysis is a type of assay for the determination of different constituents present in the coal sample. The standard procedures are followed to determine the bulk density, average particle size diameter, moisture content, volatile content, ash content, fixed carbon and surface area. Ultimate analysis gives the composition of the sample in terms of weight% of Carbon, Nitrogen, Hydrogen, Oxygen and Sulphur. The carbon content determination includes the carbon present in the organic coal substance and as mineral carbonates. Hydrogen determination gives the hydrogen content in the organic materials with the coal. All nitrogen determined is assumed to be the part of the organic materials in the coal. Table 2shows the proximate analysis for the adsorbent. Table 3 shows the physical properties of the mixed adsorbent.

**Table 2 Proximate analysis of the mixed adsorbent**

| Property | Composition of the mixed Adsorbent |
|---|---|
| Bulk Density (g/cc) | 0.74 |
| Pore Size | 572.2 nm |
| Moisture content | 3.43% |
| Volatile matter | 23.61% |
| Ash Content | 4.39% |
| Fixed carbon | 68.57% |
| Surface area ($m^2$/g) | 951 |

**Table 3Physical Properties of the mixed adsorbent**

| Adsorbent type | Surface area (m$^2$/g) | Moisture (%) | Particle size (ìm) | Charge |
|---|---|---|---|---|
| 100 % AC | 1600 | 5 | 33.29 | neutral |
| 100% BC | 267 | 3.43 | 28.40 | -ve |
| 50 % each | 951 | 4.24 | 32.44 | -ve |

**2.3 Batch Studies**

Following a systematic procedure for the removal of heavy metal ions, initially the presterilizing flasks containing heavy metal ion solution of 50 mg/l Cu (II) and Cd (II) were prepared and the mixed adsorbent of 0.25 g each (AC and BC of 1:1 ratio) was added after maintaining the desired pH. The pH was adjusted by adding 0.1M NaOH or 0.1M HCl .Adsorption process was carried out in the rotary shaker / agitator until the equilibrium. The analysis was done for the filtered samples by Atomic Absorption Spectrophotometer (AAS) to find the residual concentration in the solution. After the analysis the equilibrium time and % removal of heavy metal ions were calculated. The data obtained in the present studies were used to calculate the equilibrium metal adsorptive quantity/capacity (mg/g) by using the mass balance relationship and the percentage removal of heavy metal ions. Experiments were conducted (three repetitions) simultaneously and the average values were reported. The equilibrium metal adsorptive capacity of the metal ions ($q_e$) and % removal were calculated by using mass balance given by

$$q_e = (C_o - C_e)[\frac{V}{M}]$$

**(1)**

$$\% \, removal \, = (\frac{C_o - C_e}{C_o}) \times 100$$

**(2)**

Where $q_e$ is the amount of heavy metal ion adsorbed per unit weight of adsorbent in mg/g, V is the volume of the solution treated in liters. $C_o$, $C_e$ is the initial and equilibrium concentration of metal ions in mg/l. M is the mass of the adsorbent in grams.

**2.4 FTIR (Fourier Transform Infra-Red Spectroscopy) Analysis**

The adsorbent surface was analysed by Fourier Transform Infra-Red spectroscopy (FTIR) as shown in Figs 2 (a) (b) and (c). FTIR spectrum was obtained after 32 cumulative scans with KBr (Potassium Bromide) pellets of 1% (w/w). The pellet was subjected to FTIR (Thermo Nicolet manufactured) spectrum between wave numbers ranging from 3425-1025 cm$^{-1}$ before adsorption and 3424-510 cm$^{-1}$ after adsorption. Wave number 3600-3000 indicates the –O-H and -NH groups; Wave number 2900-2800 indicates symmetrical or asymmetrical –C-H stretching of aliphatic acids. Wave number 1700-1600 indicates –C = C (ketone group), wave number 1550-1300 indicates –C-H stretching and –C = C. Wave number 1106- 1024 and 1030 - 560: indicates C-O stretching, -C-H aromatic, miscellaneous oxides and –S-O symmetrical vibrations (weak reflectance) [7].

Fig 2 (b) and (c) indicates the FTIR Spectrum of the mixed adsorbent (Activated and Bone charcoal) after adsorption for Cu (II) and Cd (II) with different wave numbers and frequencies which have various functional groups as indicated below.
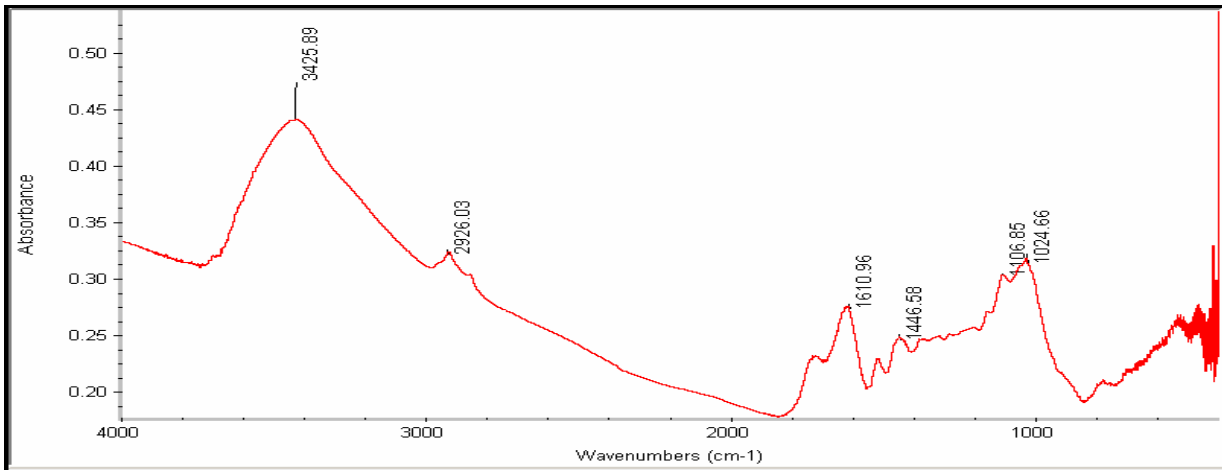
Wave number 3600-3000: -O-H and – N-H.
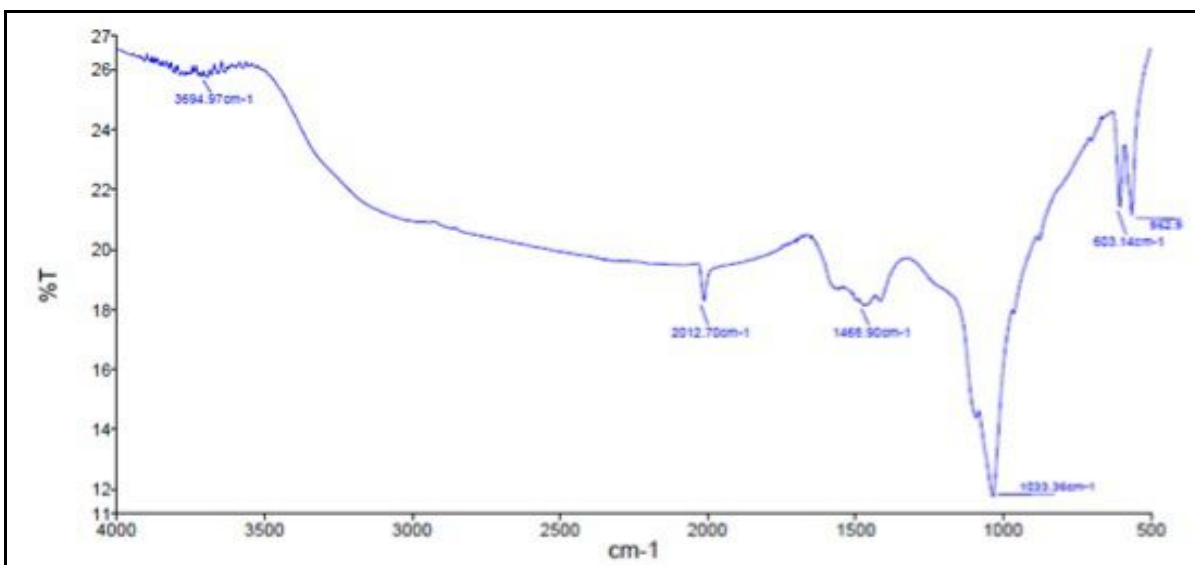Wave no: 2900-2800 Symmetrical or asymmetrical –C-H stretching of aliphatic acids
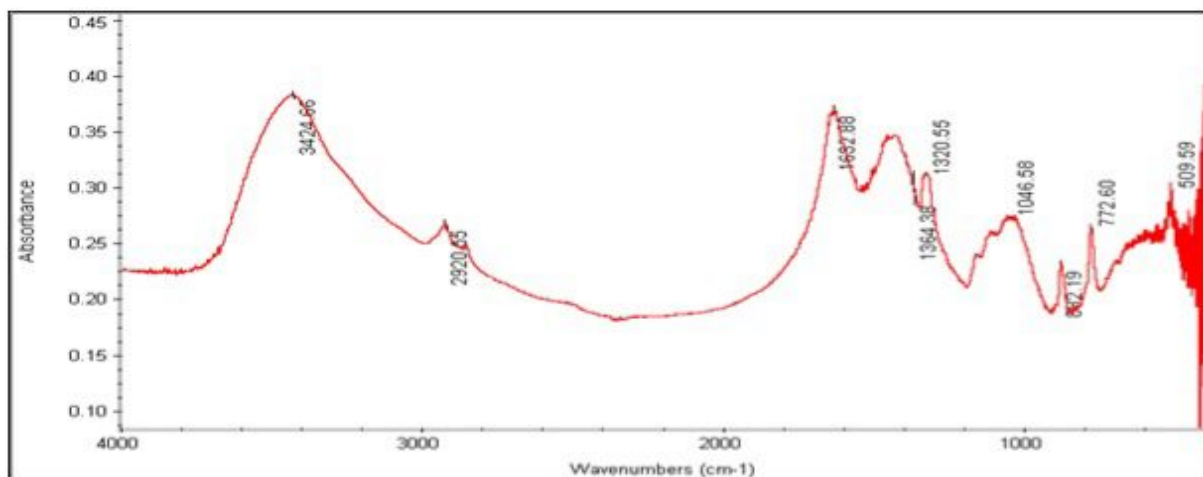Wave no: 1700-1600: -C= C
Wave no1550-1300:-C-H Stretching, -C=C.
Wave no: 1106- 1024 and 1030 - 560: C-O stretching, -C-H Aromatic, miscellaneous oxides and -S-O Symmetrical vibrations (weak reflectance) [26, 34]

**(a)  FTIR Spectrum of the mixed adsorbent (50% each) before adsorption**



**(b)  FTIR Analysis of the mixed adsorbent after adsorption for Cu**



**(c)  FTIR Analysis of the mixed adsorbent after adsorption for Cd**

**Fig 2 FTIR spectrum of mixed adsorbent (50% each before adsorption), after adsorption for Cu, after adsorption for Cd indicated as 2 (a), (b) and (c) respectively.**

**2.5 BET Analysis**

BET theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for the measurement of the specific surface area of the mixed adsorbent [8]. The specific surface area of a powder is determined by physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. Physical adsorption results from relatively weak forces (van der Waals forces) between the adsorbate gas molecules and the adsorbent surface area of the test powder. The determination is usually carried out at the temperature of liquid nitrogen. The amount of gas adsorbed can be measured by a volumetric or continuous flow procedure. The specific surface area of a powder is estimated from the amount of nitrogen adsorbed in relationship with its pressure, at the boiling temperature of liquid nitrogen under normal atmospheric pressure (Make Micrometrics Gemini 2375); Micrometrics Instrument Corporation, U.S. A (United States of America). The BET method leads to a surface area parameter which allows to compare, classify and evaluate different samples and to take into account pores (micro-, meso- and macro pores), roughnesses and particle shapes by measurement [9]. The BET surface area gets also calculated out of a complete adsorption and desorption isotherm to be used as complementary parameter for the determination of pore volume and pore size distribution. The BET surface area of the mixed adsorbent was found to be 951 $m^2$/g. (refer table 3).

# 3. Results and Discussion

## 3.1 Effect of pH

pH is one of the most important environmental factor influencing not only site dissociation but also the solution chemistry of the heavy metals, hydrolysis, complexation by organic and/or inorganic ligands [10]. Redox reactions, precipitation are strongly influenced by pH and, on the other site, strongly influence the speciation and the adsorption availability of the heavy metals. Accordingly adsorption was principally dependent on the type and ion state of the functional groups (ligands) present in the adsorbent [11]. At low pH values, the surface of adsorbent would also be surrounded by hydronium ions which decrease the metal ion interaction with binding sites of activated charcoal and bone charcoal by greater repulsive forces and therefore lower adsorption takes place. In contrast as the pH increased, the competing effect of hydrogen ions decreased and more ligands were available. Therefore at high pH values the overall surface on the activated charcoal and bone charcoal became more negative and adsorption increased. At pH higher than 8 insoluble copper and cadmium hydroxides get precipitated and restricted the true adsorption studies [12]. The experiment was conducted with the adsorbent conditions at a temperature of $25^{o}$C, 50 mg/l of initial metal ion concentration for 120 minutes with an adsorbent dose of 0.5 g of the mixed adsorbent. For Cu (II) with respect to the increase of pH the % removal increased for 50% each and the maximum % removal was 97.21% attained at 100-120 min. at pH = 6. For the cadmium with the increase of pH the % removal increased for 50% each (1:1) and the max % removal was 78.77% and attained at 120 min. At pH = 6. This huge difference in the % removal for Cu (II) and Cd (II) was due to the more atomic weight of Cd (112.411) and for Cu it is (63.546). At pH values above 8 the cadmium and copper metal ions precipitate by forming hydroxides. The results indicate that the adsorption is highly pH dependent. In the acid range the % removal of heavy metal ion increases by increasing order of pH by 6 > 4 > 2 > 8 for both the metals and in the base range it forms as hydroxide precipitate. The max % removal for Cu (II) was 97.21% and Cd (II) was 78.77 respectively obtained at 120 min & pH= 6 [13]. Figure 3 and 4 shows the effect of pH on Cu (II) and Cd (II) % removal.
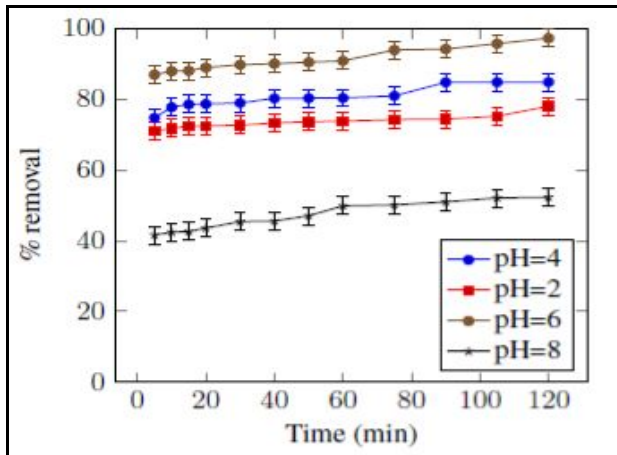
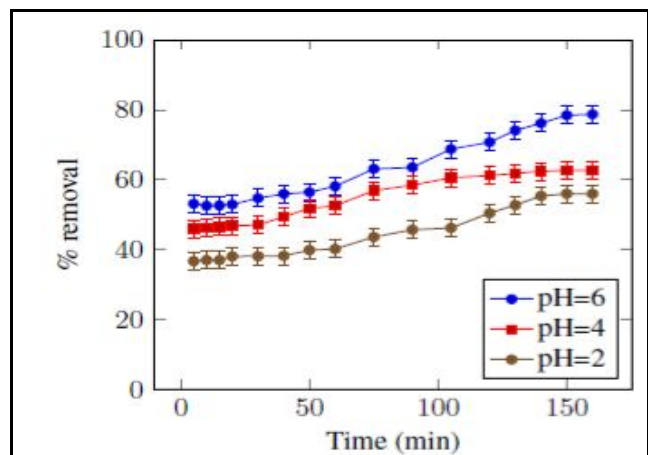**Figure 3: Effect of pH on Cu (II) % removal**



**Figure 4: Effect of pH on Cd (II) % removal**

### 3.2 Effect of Temperature

Initially the percentage removal vs sampling time follows a chemisorption process from 5- 90 min and in the later stage the % removal became almost equivalent and negligible changes have been observed from 90-120 min and further the graph approaches equilibrium in between 100-120 min and it was extended up to 150 min as shown in the fig 5. Conventionally with the increase of temperature, the adsorption decreases. However for the mixed adsorbent the overall charge being -ve the % removal of ions increases with the increase of temperature and the % removal of the heavy metal ions is highly dependent upon temperature at initial adsorption process from 5- 90 min.The % removal with respect to increase of temperature follows a chemisorption process and the maximum % removal was 99.75 at T = 40$^o$C. The % removal was almost constant at different temperature ranges between 25 to 40$^o$C and it can be predicted that the % removal is independent of temperature with respect to sampling time from 90-120 min. For the temperature range from T (40 > 35> 30 > 25) and the % removal for Cu (II) is 99.41 > 98.85 > 97.92 > 96.13 respectively and almost negligible change of removal was observed after the attainment of equilibrium as shown in the fig 5 and 6 respectively. Similarly for Cd (II) the % removal was 88.12 > 85.25 > 82.18 > 78.77 with respect to temperature T (40 > 35 > 30 > 25) was reported. The more % removal of Cu (II) was due to low atomic weight when compared to Cd (II) having higher atomic weight. The optimum temperature was found to be 40$^o$ C for both the metals. Increasing temperature likely influenced the internal structure of the adsorbent and simplified the metal ion distribution in the mixed adsorbent inter-spaces which enhances the % removal of metal ions.
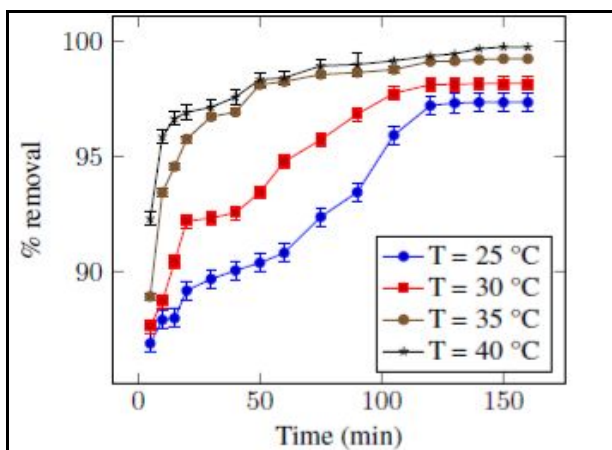


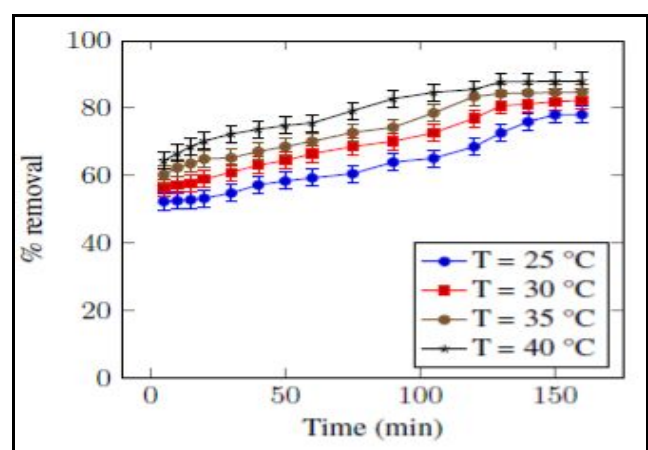**Figure 5: Effect of temperature on
Cu (II) % removal**



**Figure 6: Effect of temperature on
Cd (II) % removal**

### 3.3 Effect of adsorbent dosage

The parameter adsorbent dose is considered to be significant for effective metal ion removal as it determines sorbent- sorbate equilibrium of the system. It was observed that the amount of copper adsorbed varies with different mixed adsorbent concentration or adsorbent dose. The amount of copper adsorbed per unit mass of the mixed adsorbent decreases with an increase in adsorbent dosage from 0.5 to 5 g which determines the number of binding sites available for adsorption. The number of adsorption sites or surface area increases with the weight of adsorbent and hence results in a higher percentage removal at more dose [14]. The experiment was conducted at 25°C, 50 mg/L concentration for 5 -120 minutes at a pH of 6 for copper and cadmium.

Adsorption of metal ions on these types of materials is generally attributed to weak interactions due to physisorption and strong interactions due to chemisorption between the adsorbent and adsorbate. Due to synergistic effect the % removal increases with the increase in adsorbent dosage at the early stages of adsorption and later it got saturated at 100 min and 120 min for Cu (II) and Cd (II) respectively. Surface charges on substrates or on the mixed adsorbent as well as softness or hardness of the solutes are mostly responsible for the intensity of these interactions. Columbia interactions can be observed for the ionic exchange of cationic species with the anionic sites in the materials and is determined by their surface areas. The adsorption experiment was carried out for 0.5g, 1g, 2g, 3g and 5g of the mixed adsorbent. The % removal is highly dependent on adsorbent dosage. So the % removal increases in the order of increasing adsorbent dosage given as 5 > 3 > 2 > 1 > 0.5 g as shown in the fig 7 and 8 respectively. The experiments are carried out at pH = 6 and T = 25°C, 50 mg/l of initial concentration.  The % removal of Cu varies from 87.16 to 99.74 at 5 g, 77.46 to 92.35 at 3 g, 58.93 to 78.88 at 2 g, 52.87 to 70.13 at 1 g, and 46.9 to 60.82 at 0.5 g respectively as shown in fig 7. Similarly for Cd (II) it was 70 to 88.4 % at 5 g, 65.66 to 80.23 % at 3 g, 52.85 to 71.37 % at 2 g, 45.71 to 64.77 % at 1 g, 39.23 to 56.83 % at 0.5 g respectively as shown in the fig 8 at the same operating conditions. The optimized adsorbent dose was found to be 5 g for both the metals. The present results obtained are in correlation with the past literature results that were obtained for Cu (II) and Cd (II) removal using Granular Activated carbons, zeolites and many agricultural adsorbents [15-18].
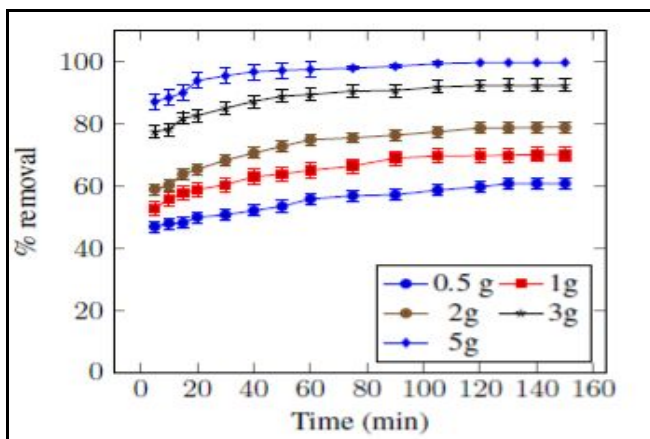

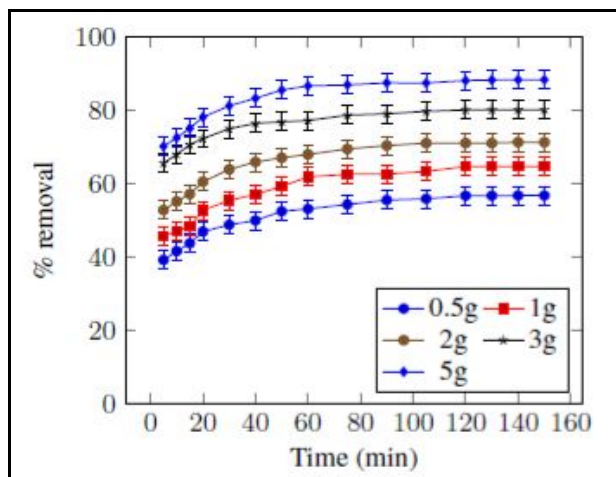
**Figure 7: Effect of adsorbent dosage on Cu (II) % removal**

**Figure 8: Effect of adsorbent dosage on Cd (II) % removal**

### 3.4     Effect of Metal Ion Concentration

It was observed from the results that at low metal ion concentrations, the ratio of surface active sites to the total metal ions in the solution is high and hence metal ions may interact with the adsorbent and can be removed from the solution. Also at high-concentration levels, some metal ion components are left unabsorbed in solution due to the saturation of binding sites on the active surface. However, amount of metal adsorbed per unit weight of adsorbent $q_e$ is higher at high concentration [19]. The experiment was conducted at a temperature of 25 °C, and at different concentrations varying from 50 to 200 mg/L and at the pH of 6 for both copper and cadmium with an adsorbent dosage of 0.5 g of the mixed adsorbent. The effect of initial metal ion concentration on the adsorption capacity shows that up to 97.21% of the Cu (II) metal ion was adsorbed at the initial metal ion concentration of 50 mg/l within first 70 minutes and later got saturated from 80- 120 min of the reaction time. As shown in the fig 9 the % removal decreases with increase in metal ion concentration from 50 to 200 ppm for Cu (II). At 100 ppm the % removal was 92.5% after attaining the equilibrium time of 120 min for the same adsorbent conditions which indicates the nearness value with a negligible difference of 4.7 %. It can be predicted that the industrial effluent whose concentration ranges between 100 to 300 ppm can be treated as an effluent and so this 100 ppm concentration can be taken as an optimized value which can be utilized in the continuous column flow operation. Similarly for cadmium with the increase of initial metal ion concentration from 50 to 100 mg/l the % removal decreases from 80.97 to 78.77 (2.2% decrement) respectively which can be negligible and there were no significant% removal were obtained at 200 ppm as shown in fig 10. This result signifies that gradual increase in the efficiency of the adsorbent shows nearness to saturation of the available binding sites. As the metal ion concentration of 150 ppm has the % removal of 77.37 and 64 % for Cu and Cd (II) respectively, hence so it can be taken as an intermediate between 100 and 200 ppm. It can be concluded that there is a negligible % removal of 2.2% as shown above between 50 ppm and 100 ppm concentrations so the same 100 ppm IMC can be used in the continuous column flow operation for both Cu and Cd metal ion. The optimized Initial metal concentration was obtained as 100 ppm for both the divalent metals. The present results obtained are in correlation with the past results obtained from the literature. [20, 21-22]. Figure 9and 10 shows the effect of Metal ion concentration on Cu (II) and Cd (II) % removal respectively.
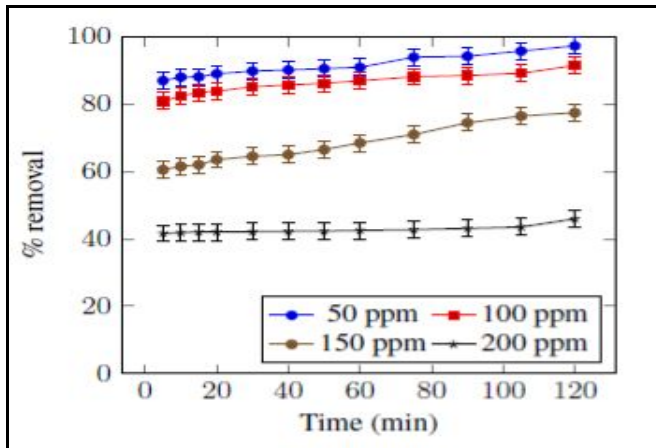
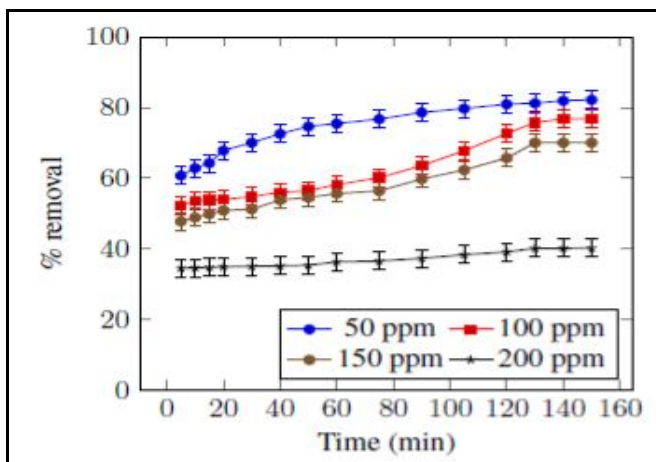**Figure 9: Effect of Metal ion concentration on Cu (II) % removal**



**Figure 10: Effect of Metal ion concentration on Cd (II) % removal**

### 3.5    Effect of Agitation rate

Agitation was an important parameter in adsorption because it helps in overcoming the external mass transfer resistance. At higher agitation rate the mass transfer resistance related to ion diffusion through the liquid film surrounding the mixed adsorbent was reduced as the film thickness reduces due to more shaking speed or agitation rate which results in metal ion uptake. Agitation of the solution not only results in a decrease in film transfer resistance but also results in the abrasion of the mixed adsorbent and produces the freshly broken and highly reactive locations on the adsorbent surface. So this mechanical effect increases the number of possible adsorption locations/sites that results in an increase in the rate of adsorption. However, the production of fine particles due to abrasion has its disadvantages, which becomes increasingly difficult to separate the solute/solids from the liquid [23]. The experiment was conducted with the adsorbent conditions 50 mg/l of metal ion concentration and 5 g of mixed adsorbent for 120 minutes at the pH 6 for both copper and Cadmium. As agitation rate was an important factor in adsorption for the batch study for the heavy metal ions, it can be concluded that the more mass transfer can takes place during the reaction/agitation at higher agitation rate of 180 rpm when compared to low agitation rate of 60 rpm. Due to the turbulence effect the % removal increases with the increase of agitation rate for the mixed adsorbent. The % removal increases with the increase of agitation rate (rpm) and the order is as follows: 180 > 150 > 120 > 90 > 60 rpm. The optimized agitation rate was found to be 180 rpm for both the metals. The maximum % removal was 92% and 86.9% at 180 rpm for Cu (II) and Cd (II) respectively as shown in Fig 11 and 12.
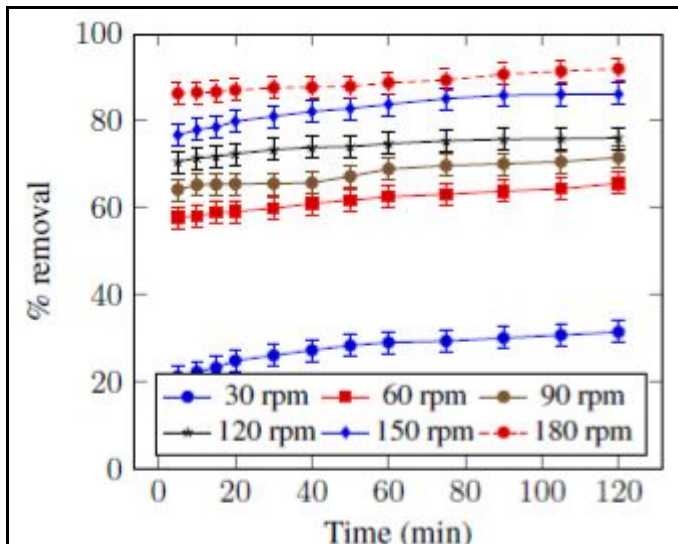
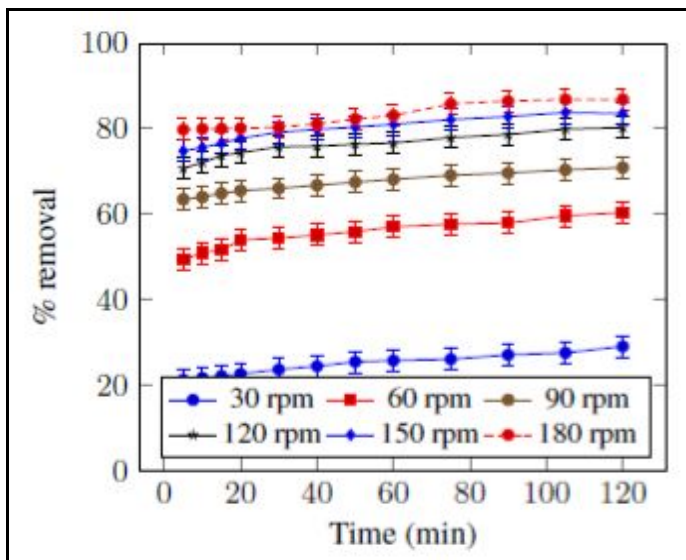**Figure 11: Effect of Agitation rate on Cu (II) % removal**



**Figure 12: Effect of Agitation rate on Cd (II) % removal**

### 3.6 Effect of Contact time

The outcome acquired from the contact time demonstrates that the rate of adsorption increases /rises with the increment of contact time between the adsorbent and metal particle or adsorb ate arrangement in the solution. After certain amount of time all the active sites of the adsorbent were filled either with metal ions or the solution itself was saturated. So increase in rate of adsorption ceases and percentage removal becomes constant and approaches a saturation point [23]. The experiment was conducted with the adsorbent conditions at 50 mg/L of Initial Metal ion Concentration (IMC) and 5 g of the mixed adsorbent at pH 6 for copper and cadmium metal ions with an agitation rate of 180 rotations per minute (RPM) and contact time varying from 5 to 120 minutes respectively. It can be concluded that with respect to increase of contact time the % removal increases and the optimized contact time for Cu (II) with 50 % each is 105 to 120 min where (94.83% removal) was reported at pH 6. Similarly for Cd (II) the optimized contact time with 50% each was 120 -130 min where the % removal was reported as (76.88-77.35%) at pH 6 that are shown in Fig 13 and 14 respectively.
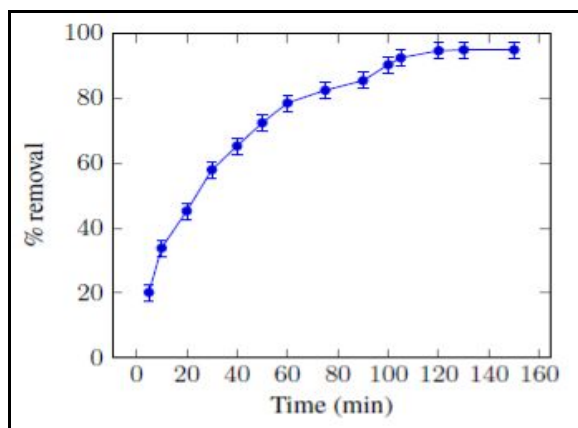
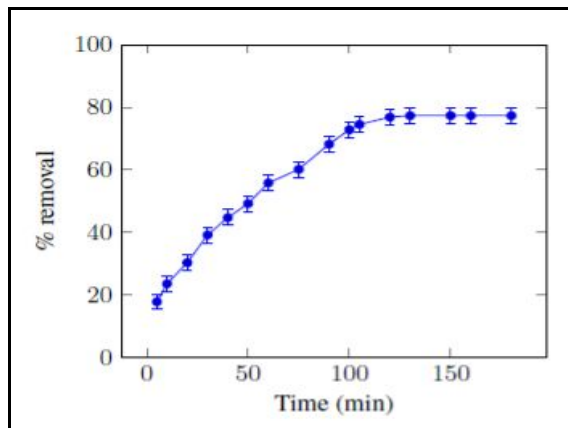**Figure 13: Effect of Contact time on Cu (II) % removal**



**Figure 14: Effect of Contact time on Cd (II) % removal**

## 4.　Conclusions

Experiments were conducted to investigate the copper and cadmium removal from the aqueous solution by the mixed adsorbent prepared by blending activated charcoal and bone charcoal in 1:1 ratio. Approximately above 99% of the copper and 88-90% of the cadmium ions originally present in the solution were adsorbed onto the mixed adsorbent within 100-120 minutes after the start of the adsorption experiments and equilibrium was reached within 2 hours for both the metals. The maximum adsorption capacity of Cadmium was 6.71 mg/g at the optimized pH 6, with the adsorbent dosage of 0.5 gm. Incase of initial metal ion concentration (IMC) and temperature, the maximum adsorption capacity $Q_{max}$ (Adsorption capacity) was 19.64 mg/g at 150 ppm and 8.34 mg/g at $40^{o}$C respectively for Cd (II). The maximum adsorption capacities of Copper were 9.44 mg/g at the optimized pH 6, with an adsorbent dosage of 0.5 gm. In case of the parameters Metal Ion Concentration (MIC) and temperature the maximum adsorption capacity $Q_{max}$ was 22 mg/g at 150 ppm and 9.64 mg/g at $40^{o}$C respectively for Cd (II). The order of affinity for Cu (II) was greater than Cd (II) due to the lower atomic weight of Cu (63.5 g/gmole) than that of Cd (112.4 g/gmole).

## Abbreviations

MIC -Metal Ion Concentration
IMC -Initial metal ion concentration
RPM -Rotations per minute
U.S. A - United States of America
FTIR – Fourier Transform Infrared Spectroscopy
AAS- Atomic Absorption Spectrophotometer
DLS - Dynamic Light Scattering
PCS- Photon Correlation Spectroscopy
AC - Activated Charcoal AC
BC -Bone charcoal
50 % each (1:1 ratio of AC + BC)
$Q_{max}$- Maximum Adsorption capacity

**Conflict of Interests** The authors declare that they have no conflict of interests.

**Declaration by the Authors**

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## References

1. Olga Freitas, Cristina Delerue-Matos, and Rui Boaventura., Kinetic and Thermodynamic Studies of the Biosorption of Cu ( II ) by Agaricus campestris., Journal of Physical Chemistry., 2011, 30(2), 177–186.
2. Z Yao, J Qi, and LWang., Equilibrium, kinetic and thermodynamic studies on the biosorptionof Cu (II) onto chestnut shell., Journal of Applied surface science., 2010, 174, 137–143.
3. S. Kalyani, P Srinivasa Rao, and A. Krishnaiah., Removal of nickel (II) from aqueous solutions using marine macro algae as the sorbing biomass., Chemosphere., 2004, 57, 1225–1229.
4. Shaobin Wang, Yuelian Peng., Natural zeolites as effective adsorbents in water and wastewater treatment., Chemical Engineering Journal.,2010, 156, 11–24.
5. WANG Yasong, XU Yunpeng, TIAN Zhijian, LIN Liwu., Research Progress in Ion thermal Synthesis of Molecular Sieves., Chinese Journal of Catalysis., 2012, 33, 39–50.
6. I.A Sengil, and M. Ozacar., Biosorption of Cu (II) from aqueous solutions by mimosa tannin gel., Journal of Hazardous Materials., 2008, 157, 277-285.
7. P.D Johnson, M.AWatson, J.Brown, I.A. Jefcoat. Peanut hull pellets as a single use sorbent for the capture of Cu (II) from waste water., Waste Management., 2002, 22(5), 471-480.
8. J.R Rangel-Mendez, M.H Tai, M. Streat.,Removal of cadmium using electrochemically oxidized activated carbon., Process Safety and Environmental Protection., 2000, 78(2), 143–148.
9. G Akkaya, F Guzel., Bioremoval and recovery of Cu (II) and Pb (II) from aqueous solution by a novel biosorbent watermelon (citrullus lanatus) seed hulls: Kinetic study, equilibrium isotherm, sem and FTIR analysis., Desalination and Water Treatment.,2009, 51, 7311–7322.
10. D.T.B Keerthiratn, S Thushara, A Priyantha, N Tennakoon., Removal of heavy metal ions from polluted water using environmentally friendly materials. Journal of European Sciences.,2000, 48, 300–309.
11. M. Birch., Properties influencing the specific surface areas of carbon nanotubes and Nano fibers., Journal of Analysis of Occupation and Hygiene., 2013, 57 (9), 1148-1166.
12. P. Pavasant, R. Apiratikul, V. Sungkhum, P. Suthiparinyanont, S.Wattanachira, T.F.Marhaba., Biosorption of $Cu^{2+}$, $Cd^{2+}$, $Pb^{2+}$ and $Zn^{2+}$ using dried marine *green macro alga caulerpa Lentilligera*., Journal of Bioresource Technology., 2013, 97 (2), 2321-2329.
13. P.Vasudevan, V. Padmavathy, S.C Dhingra., Kinetics of Biosorption of Cadmium on Baker's yeast., Journal of Bioresource Technology.,2003, 89 (3), 281-287.
14. A. Hanif, H. Nawaz Bhatti, M. Asif Hanif., Removal and Recovery of Cu (II) and Zn (II) Using Immobilized *Mentha Arvensis* Distillation Waste Biomass.,*Journal of* Ecological *Engineering.,2009,* 35 (10), 1427-1434.
15. M. Nora Hilal, A. Inas Ahmed, E. Ragaa, E.L. Sayed., Activated and non-activated date pits adsorbents for the removal of Copper (II) and Cadmium (II) from aqueous solutions,International Scholarly Research Network ISRN. Journal of Physical Chemistry., 2000, 48, 300–309.
16. K. Karunakaran,R. Thamilarasu Sharmila., Kinetic equilibrium and thermodynamic studies on removal of Cr (VI) by modified activated carbon prepared from Ricinus Communes seed shell. Coromandal Journal of Science, 2012, 1: 30–39
17. S. Bable, T.A Kurniawan., Low-cost adsorbent for heavy metals uptake from contaminated water -A review Journal of Hazardous Materials., 2003, 97, 219–243.
18. M.A Awan, A. Ishtiaq, I.Khalid., Removal of heavy metals through adsorption using sand., Journal of Environmental Sciences., 2003, 15 (3), 413–416.
19. A. Ozer, D. Ozer., The adsorption of copper (II) ions on to dehydrated wheat bran (DWB): Determination of equilibrium and thermodynamic parameters., Process Biochemistry., 2004, 39, 2183–2191.
20. H. Ahsan, N. Islam, A.Islam, A.M. Shafiqul Alam., Removal of copper from aqueous solution using orange peel, sawdust and bagasse., Pakistan Journal of Analytical and Environmental Chemistry., 2007, 8 (1), 21–25.
21. I. Semra, N. Macit, K. Serpil, O. Huseyin., Removal of chromium, lead and copper ions from industrial waste water by staphylococcus saprophyticus., Turkish Electronic Journal of Biotechnology., 1998, 2, 50–57.
22. O. Innocent, A. Emmanuel, A. Thomas., Biosorption of heavy metal ions from aqueous solutions using a biomaterial., Leonardo Journal of Sciences., 2009., 14, 58–65.

23. C. A. Toles, W.E.Marshall, M. M. Johns., Surface functional groups on acid activated nutshells. Carbon Journal of Carbon Chemistry., 1999, 37, 1207–1214.

24. B. Volesky., Biosorbents for the metal recovery and their trends., Journal of Biotechnology., 1987, 5, 96–101.

25. K. Amela, H. Abdeslam, M.D. Kerroum., Isotherm and kinetic study of biosorption of cationic dye onto banana peel., Energy Procedia., 2013, 19, 286–295.

26. R.Sudha, P. Premkumar, Lead Removal by Waste Organic Plant Source Materials Review, International Journal of ChemTech Research,2016, Vol.9, No.01 pp 47-57.

27. Kouame Kouame Victor, Meite Ladji, Adjiri Oi Adjiri, Yapi Dope Armel Cyrille, Tidou Abiba Sanogo, Bioaccumulation of Heavy Metals from Wastewaters (Pb, Zn, Cd, Cu and Cr) in Water Hyacinth (*Eichhornia crassipes*) and Water Lettuce (*Pistia stratiotes*), International Journal of ChemTech Research ,2016, Vol.9, No.02 pp 189-195.

28. Senthamil Selvan K, Palanivel M, A Case study approach on Municipal Solid Waste generation and its impact on the soil environment in Dharapuram Municipality, Tamilnadu, India, International Journal of ChemTech Research,2016, Vol.9, No.02 pp 196-204.

29. M. Mohamed Sihabudeen, A. Abbas Ali and A. Zahir Hussain, Removal of Heavy Metals from Ground Water using Eucalyptus Carbon as Adsorbent, International Journal of ChemTech Research ,2016, Vol.9, No.03 pp 254-257.

30. G.BabuRao, M. Krishna Prasad, K. Kishore Kumar, Biosorption of Copper (II) from Aqueous Solution using Oscillatoria.Splendida, International Journal of ChemTech Research,2016, Vol.9, No.03 pp 290-295.

31. Naga Babu, G.V. Krishna Mohan and K. Ravindhranath, Removal of Chromium (VI) from Polluted waters using Adsorbents derived from Chenopodium album and Eclipta prostrate Plant Materials, International Journal of ChemTech Research , 2016, Vol.9, No.03 pp 506-516.

32. Ankita Chatterjee and Jayanthi Abraham; Biosorption Capacity of Dried Spirogyra on Heavy Metals; International Journal of ChemTech Research;2015, Vol.8, No.9 pp 387-392.

33. Vilas Y. Sonawane; Analysis of Heavy metals in vegetables collected from selected area around Dhulia, North Maharashtra, Maharashtra, India;2015, Vol.8, No.4, pp 1935-1939.

34. V.L.Nirmal Bhargavi, P.N.Sudha; Removal of heavy metal ions from soil by electrokinetic assisted phytoremediation method; International Journal of ChemTech Research;2015, Vol.8, No.5, pp 192-202.

35. Lina Rose Varghese and Nilanjana Das; Application of nano-biocomposites for remediation of heavy metals from aqueous environment: An Overview; International Journal of ChemTech Research;2015, Vol.8, No.2, pp 566-571.

36. Ahmed Hassan Alamin, Lupong Kaewsichan; Adsorption of Zn(II) and Cd(II) ions from aqueous solutions by Bamboo biochar cooperation with Hydroxyapatite and Calcium Sulphate; 2015, Vol.7, No.5, pp 2159-2170.

37. K. Sangeetha, G. Vasugi, E. K. Girija; Removal of lead ions from aqueous solution by novel hydroxyapatite/alginate/gelatin composites; International Journal of ChemTech Research;2015, Vol.8, No.5, pp 117-125.

38. Farida S. E. El-Dars, Hanan S. Ibrahim, Bahaa A. Salah, Hani M. Mehanna, Nabila S. Ammar and Abdel Rahman H. Saleh; The Proficiency of Different Mature Compost in Suppressing the

39. Uptake of Heavy Metal by *Jatropha curcas* L., Castor Bean and Sunflower Plants; International Journal of ChemTech Research;2015, Vol.8, No.12 pp 178-186.

40. Archana S and Jaya Shanthi R, Removal of Cr (VI) from tannery effluent using synthesized polyphenylenediamine nanocomposites; International Journal of ChemTech Research;2015, Vol.8, No.5, pp 85-89.

41. Jenela Priscy. J and Reya Issac. I; Comparitive Studies for the Adsorption of Cadmium and Chromium from Aqueous Solution using Stalk of Solanum Melongena and Abelmoschus Esculentus; International Journal of ChemTech Research;2015, Vol.8, No.11 pp 539-547.

42. M Mohammad Athiq, Abhishek. B, Saranya D, Rohit KC, Prashanth Kumar HP; Application of Bio technology in Treatment of Heavy Metal Contaminated Industrial Waste Water-A case study; International Journal of ChemTech Research; 2015, Vol.8, No.5, pp 144-147.

43. S. Malathi, K.Srinivasan and M.Gomathi; Studies on the removal of Cr (VI) from aqueous solution by activated carbon developed from Cottonseed activated with sulphuric acid; International Journal of ChemTech Research;2015, Vol.8, No.2, pp 795-802.

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